

67,200-1130  
2002-1331

## METHOD FOR CLEANING SUBSTRATES USING SUPERCRITICAL FLUIDS

### Field of the Invention

[001] The present invention relates to methods for cleaning substrates. More particularly, the present invention relates to methods for cleaning substrates using a supercritical cleaning fluid.

### Background of the Invention

[002] In the fabrication process for semiconductor devices, numerous fabrication steps, as many as several hundred, must be executed on a silicon wafer in order to complete integrated circuits on the wafer. Generally, the process for manufacturing integrated circuits on a silicon wafer substrate typically involves deposition of a thin dielectric or conductive film on the wafer using oxidation or any of a variety of chemical vapor deposition processes; formation of a circuit pattern on a layer of photoresist material by photolithography; placing a photoresist mask layer corresponding to the circuit pattern on the wafer; etching of the circuit pattern in the conductive layer on the wafer; and stripping of the photoresist mask layer from the wafer. The wafer is typically subjected to a polishing operation to provide an extremely level starting surface on the wafer. During the subsequent structuring of the substrate, the

67,200-1130  
2002-1331

various processing steps are used to build up layers of conductors and dielectrics, for example, on which other layers are formed to fabricate the circuits. With structuring becoming ever finer, the associated replication processes are becoming more sensitive to surface variations on the substrate. Therefore, it has now become necessary to "re-level" the wafer surface even while production of the integrated circuits are in progress. The re-leveling operation is referred to as planarizing and is typically accomplished using the CMP (chemical mechanical planarization) method using a chemical mechanical polishing process.

[003] In chemical mechanical polishing, an abrasive suspension agent or slurry is dispensed onto a polishing surface. Relative movement between the polishing surface and the wafer produces a combined mechanical and chemical effect on the surface of the wafer. This process creates a highly level surface on the wafer. In order to remove the still-moist remains of slurry, as well as small surface defects which may remain in the wafer and disrupt the otherwise planar continuity of the wafer surface after the CMP process, post-CMP cleaning steps are required.

[004] In semiconductor production, the quality of the

67,200-1130  
2002-1331

integrated circuits on the semiconductor wafer is directly correlated with the purity of the fabricating processes, which in turn depends upon the cleanliness of the manufacturing environment. Furthermore, technological advances in recent years in the increasing miniaturization of semiconductor circuits necessitate correspondingly stringent control of impurities and contaminants in the plasma process chamber. When the circuits on a wafer are submicron in size, the smallest quantity of contaminants can significantly reduce the yield of the wafers. For instance, the presence of particles during deposition or etching of thin films can cause voids, dislocations, or short-circuits which adversely affect performance and reliability of the devices constructed with the circuits.

[005] One of the cleaning steps carried out after the chemical mechanical polishing process is facilitated using scrubber brushes. Accordingly, a special washing fluid and a rotational movement with multiple pairs of scrubber brushes can clean both sides of the wafer using contact pressure against the wafer. Because the wafer becomes considerably more valuable with each successive planarizing operation, the post-CMP brush cleaning operation is commercially significant.

67,200-1130  
2002-1331

[006] After brushes have been applied to the wafer, the wafer is transported into a spin, rinse and dry (SRD) station. In the SRD station, de-ionized water is sprayed onto the surface of the wafer while the wafer is spun at speeds of between about 100 and 400 revolutions per minute. The wafer is then spun to dry, after which processing of the wafer resumes.

[007] The post-CMP scrubber brush method for removing particles and remaining surface defects from the surface of a planarized wafer is attended by several disadvantages, one of the foremost being that the scrubber brush has a tendency to trap and become contaminated with the larger particles removed from the wafer. Consequently, the trapped particles may potentially become dislodged from the scrubber brush upon cleaning and planarization of a subsequent wafer. The presence of particles in the integrated circuits compromises the functional integrity of the devices in the finished electronic product.

[008] A common disadvantage inherent in the rinsing and drying of wafers in an SRD station is that electric potentials induce galvanic corrosion in metal lines on the wafer when copper lines on the P+ region and the N+ region behave as anode and cathode, respectively. This galvanic corrosion phenomenon

67,200-1130  
2002-1331

is enhanced by the heating lamp in the SRD station, which generates electron-hole pairs in the depletion region of the P/N junction. Accordingly, a new and improved method is needed for cleaning wafers and which avoids the drawbacks inherent in scrubber brush cleaning and spin-rinse-dry cleaning.

[009] An object of the present invention is to provide a new and improved method of cleaning substrates.

[0010] Another object of the present invention is to provide a new and improved method which is suitable for removing residues from substrates after a chemical mechanical polishing (CMP) operation.

[0011] Still another object of the present invention is to provide a new and improved substrate cleaning method which prevents or substantially reduces galvanic corrosion of metal lines on semiconductor wafer substrates.

[0012] Yet another object of the present invention is to provide a new and improved substrate cleaning method which includes the use of a supercritical cleaning fluid to remove residues from the substrate.

67,200-1130  
2002-1331

[0013] A still further object of the present invention is to provide a new and improved substrate cleaning method which is self-drying.

[0014] Yet another object of the present invention is to provide a new and improved substrate cleaning method which is capable of utilizing any of a variety of supercritical cleaning fluids to remove residues from a substrate.

#### Summary of the Invention

[0015] In accordance with these and other objects and advantages, the present invention is generally directed to a new and improved method for cleaning substrates typically after a CMP process is carried out thereon. The method includes providing a cleaning chamber, providing a substrate to be cleaned in the cleaning chamber, providing the chamber at temperature and pressure conditions favorable for formation of a supercritical cleaning fluid therein, and introducing the liquid or gaseous fluid into the chamber to form the supercritical cleaning fluid therein. The supercritical fluid removes particles and residues from the substrate without causing the formation of voltage potentials which may otherwise cause galvanic corrosion of metal lines or other device features on

67,200-1130  
2002-1331

the substrates in the case of wet-cleaning applications. Suitable cleaning fluids which are capable of being used as the supercritical fluid include methane, ethane, propane, carbon dioxide, ammonia, nitric oxide, fluoromethane and difluoromethane.

#### Brief Description of the Drawings

[0016] The invention will now be described, by way of example, with reference to the accompanying drawings, in which:

[0017] FIG. 1 is a schematic of an illustrative cleaning system suitable for implementation of the method of the present invention;

[0018] FIG. 2 is a flow diagram illustrating a typical flow of process steps according to the method of the present invention;

[0019] FIG. 3A is a cross-section of a substrate in one application of the method of the present invention;

[0020] FIG. 3B is a cross-section of a substrate in another application of the method of the present invention; and

67,200-1130  
2002-1331

[0021] FIG. 4 is a schematic of an illustrative cleaning system in implementation of the method of the present invention.

#### Description of the Preferred Embodiments

[0022] The present invention has particularly beneficial utility in the removal of particles and residues from substrates after the substrates are subjected to chemical mechanical polishing or planarization (CMP). However, the invention is not so limited in application and while references may be made to CMP processes, the method of the invention is more generally applicable to cleaning substrates in a variety of industrial applications.

[0023] The present invention is directed to a new and improved method for the cleaning of substrates using supercritical cleaning fluids. The method eliminates the need for wet cleaning of substrates which may otherwise form conductive circuits on and resultant galvanic corrosion of metal lines and other conductive device components. Furthermore, the supercritical cleaning fluid cleans the substrate without the mechanical abrasion which characterizes most scrubber brush cleaning methods.

[0024] A variety of cleaning fluids may be used according to the method of the present invention. These include methane,

67,200-1130  
2002-1331

ethane, propane, carbon dioxide, ammonia, nitric oxide, fluoromethane and difluoromethane. At various critical temperatures and pressures, these fluids move from a liquid or gaseous phase to a supercritical phase. The critical temperatures and pressures under which these various fluids become operational for purposes of the invention are shown in Table I below.

Table I

Cleaning Fluid	Critical Temperature (C)	Pressure (Bar)
Methane	-82.4	46
Ethane	32.4	48.8
Propane	96.7	42.5
Carbon dioxide	31.1	73.8
Ammonia	132.4	113.5
Nitric oxide	36.6	72.4
Fluoromethane	42.0	56.0
Difluoroethane	78.6	58.3

[0025] Carbon dioxide exists in the supercritical state at a temperature range of from about 350° K to about 450° K, and at a pressure range of from about 0 psi to about 6000 psi.

[0026] The cleaning fluid is typically mixed with a solvent prior to forming the supercritical cleaning fluid from the

67,200-1130  
2002-1331

liquid or gas cleaning fluid. Examples of suitable solvents in this regard include isopropyl alcohol or other alcohols, ethylene glycol, hydrogen fluoride or ammonium hydroxide, in non-exclusive particular.

[0027] Referring initially to FIG. 1, an example of a cleaning system which is suitable for implementation of the present invention is generally indicated by reference numeral 10. The cleaning system 10 includes a cleaning fluid holding tank 12 which holds a supply of cleaning fluid 14 in either the liquid or gaseous state. A holding tank outlet conduit 16, having a pump 18, leads from the cleaning fluid holding tank 12 to a mixing conduit 20. The mixing conduit 20 leads from a solvent holding tank 22 which contains a supply of solvent 23. A pump 24 is provided in the mixing conduit 20.

[0028] The mixing conduit 20 leads into a cleaning chamber 28 that contains a substrate support 30. The cleaning chamber 28 is provided with a heating and cooling system, as well as a pressurization system, to provide wide fluctuations in both temperature and pressure inside the cleaning chamber 28, according to the knowledge of those skilled in the art. A chamber outlet conduit 36, having a pump 38, leads from the cleaning chamber 28 and communicates with a recycle system 40.

67,200-1130  
2002-1331

An exhaust conduit 42, having a pump 46, leads from the recycle system 40 and is provided in fluid communication with an exhaust unit 44. A return conduit 50 having a pump 52 leads from the recycle system 40 and is provided in fluid communication with the cleaning fluid holding tank 12.

[0029] Referring again to FIG. 1, typical operation of the cleaning system 10 according to the method of the present invention is as follows. A substrate 32 to be cleaned is initially placed on the substrate support 30 inside the cleaning chamber 28. The substrate 32 may be a post-CMP substrate, for example, having CMP residues thereon which must be removed from the substrate prior to further processing. The substrate 32 typically includes an exposed N-doped region, P-doped region and conductive layer. A cleaning fluid 14 is contained in the cleaning fluid holding tank 12 at the appropriate temperature to maintain the cleaning fluid 14 in either the liquid or gaseous state. For example, the methane, ethane, propane, carbon dioxide or nitric oxide cleaning fluid 14 may be maintained as a pressurized gas in the cleaning fluid holding tank 12. The fluoromethane or difluoromethane cleaning fluid 14 may be maintained as a liquid in the cleaning fluid holding tank 12.

[0030] After the substrate 32 is placed on the substrate

67,200-1130  
2002-1331

support 30 and the cleaning fluid 14 is provided in the cleaning fluid holding tank 12, the cleaning chamber 28 is set at the temperature and pressure conditions that are required to transform the cleaning fluid 14 from the liquid or gaseous state to the supercritical fluid state, and these threshold temperature and pressure conditions vary according to the cleaning fluid used, as shown in Table I. By operation of the pump 18, the cleaning fluid 14 is then pumped from the cleaning fluid holding tank 12, through the holding tank outlet conduit 16 and into the mixing conduit 20. Simultaneously, by operation of the pump 24, the solvent 23 is distributed from the solvent holding tank 22 and into the mixing conduit 20. As they are pumped through the mixing conduit 20, the cleaning fluid 14 and the solvent 23 mix together to define a cleaning fluid/solvent mixture 26 that enters the cleaning chamber 28.

[0031] As the cleaning fluid/solvent mixture 26 enters the cleaning chamber 28, the cleaning fluid therein reaches the supercritical temperature and pressure which transform it from the liquid or gaseous state to the supercritical state, at which point the cleaning fluid forms a supercritical cleaning fluid 34. The supercritical cleaning fluid 34, which is typically non-conductive, contacts the substrate 32 and removes particles and other residues remaining from the CMP or other process

67,200-1130  
2002-1331

therefrom. Typically, the supercritical cleaning fluid 34 remains in the cleaning chamber 28 for a period of typically about 5-10 minutes, at which point substantially all of the particles and other residues have been removed from the substrate 32 by the supercritical cleaning fluid 34. At that point, the pump 38 is operated to draw the supercritical cleaning fluid 34, along with the particles and residues removed from the substrate 32, from the cleaning chamber 28, through the chamber outlet conduit 36 and into the recycle system 40. In the recycle system 40, the particles and other residues are removed from the supercritical cleaning fluid 34 and the supercritical cleaning fluid 34 is heated or cooled to transform it back to the liquid or gaseous state. Exhaust fluid 48 may be discharged through the exhaust conduit 42 and the exhaust unit 44 by operation of the pump 46. The rest of the gaseous or liquid cleaning fluid 14 is returned to the cleaning fluid holding tank through the return conduit 50, by operation of the pump 52. The cleaning chamber 28 is then returned to normal temperatures and pressures for removal of the substrate 32 from the substrate support 30 and the cleaning chamber 28 to resume processing of the substrate 32.

[0032] The flow diagram of FIG. 2 summarizes a typical flow of process steps according to the method of the present

67,200-1130  
2002-1331

invention. In process step S1, a substrate is placed typically on a substrate support inside a cleaning chamber. In process step S2, the cleaning chamber is set at the temperature and pressure necessary to transform the cleaning fluid from the liquid or gaseous state to the supercritical state. This temperature and pressure varies according to the cleaning fluid used. In process step 3, the solvent is introduced into the liquid or gaseous cleaning fluid and mixed. In process step 4, the cleaning fluid/solvent mixture is introduced into the cleaning chamber, at which point the cleaning fluid is transformed from the liquid or gaseous state to the supercritical state, due to the supercritical temperature and pressure set in the cleaning chamber. In process step 5, the supercritical cleaning fluid contacts the substrate and removes particles and residues from the substrate.

[0033] Referring next to Figure 3A, a substrate 300 is provided. The substrate may be a semi-conducting substrate with a dielectric layer 302 deposited on top. The dielectric layer 302 can be SiO<sub>2</sub> deposited using a TEOS process. Subsequently, photolithography and etching steps are used to define the dielectric layer forming a trench 304. A conductive metal layer 306 is then deposited in the trench and on top of the dielectric layer. The conductive metal layer may be Cu or W. The

67,200-1130  
2002-1331

conductive layer is planarized to form multiple metal conductive lines. CMP slurry solution or particles may be left on the substrate during the CMP planarization process.

[0034] Referring now to Figure 4, the substrate 300 is placed in a supercritical cleaning chamber 208 of a supercritical cleaning system 204. Subsequently, carbon dioxide 214 is flown from a first holding tank 200 through a first conduit 202 that connects to a second holding tank 204 through a second conduit 203. The second holding tank 204 holds a chemical substance 190 that increases the solubility of the carbon dioxide 214, by actuation of a first pump 206 of the first conduit 202 to flow a carbon dioxide/chemical substance mixture 226 into the supercritical cleaning chamber 208 at a flow rate of 0.2-0.6 liter/min. The pressure in the first holding tank 200 is 25-35 ATM, and the temperature is room temperature, while the carbon dioxide 214 is supplied in a liquid state. A second pump 207 is in fluid communication with the second storage tank 204 for pumping the chemical substance 190 to improve solubility of the carbon dioxide 214 into the supercritical cleaning chamber 208 in order to increase the cleaning capacity of the carbon dioxide 214. The chemical substance 190 that improves the solubility of the carbon dioxide 214 may be methanol,  $H_2O_2$ , benzene or other non-conductive additives.

67,200-1130  
2002-1331

[0035] The flowing process for the carbon dioxide 214 into the supercritical cleaning chamber 208 is continued until the carbon dioxide 214 fills up the cleaning chamber 208. The pressure and temperature are increased in the supercritical cleaning chamber 208 such that the carbon dioxide 214 in the supercritical cleaning chamber 208 is maintained in a supercritical state: at a temperature of 310-500 degrees C and a pressure of 1500-1000 psi. The density of the carbon dioxide 214 in the supercritical cleaning chamber 208 is 500-900 kg/m<sup>3</sup>. The carbon dioxide 214 in the supercritical cleaning chamber 208 circulates inside the chamber 208 to improve the cleaning effect. The circulation speed inside the chamber 208 is 0.5-3 meter/sec.

[0036] After the cleaning process is completed, the spent carbon dioxide 214a is flown through a third conduit 210, which connects the supercritical cleaning chamber 208 to a recycle system 212, into the recycle system 212, by actuation of a pump 211. Re-usable carbon dioxide 214b is flown through a fifth conduit 215 that connects between the recycle system 212 and the first storage tank 200 and pumped by the fourth pump 222 into the first storage tank 200 for continued use. The un-usable carbon dioxide 214c is flown through a fourth conduit 225 that

67,200-1130  
2002-1331

connects between the recycle system 212 and a heated exhaust system 216 and pumped by the third pump 220 into the heated exhaust system 216 for exhausting. After the cleaning steps are completed, the substrate 300 is removed from the cleaning chamber 208 wherein the metal surface of the substrate 300 is cleaned by the supercritical cleaning procedure and the contaminating particles produced during the planarization of the conductive layer are removed.

[0037] The second implementation example is shown in Figure 3B, wherein a substrate 300 that has multiple metal conducting lines 312, which may be formed of copper, is provided. An upper dielectric layer 314 is then deposited on top of the metal conducting lines. The upper dielectric layer 314 may be formed of  $\text{SiO}_2$  by TEOS chemistry. Known technologies of photolithography and etching are then used to define the upper dielectric layer forming a conductive line contact window 316. During the photolithography and etching processes, the surface of the substrate 300 is deposited with residual photoresist material, particles, or conglomerates.

[0038] Referring again to Figure 4, the substrate 300 is placed in a supercritical cleaning chamber 208 of the supercritical cleaning system 204. Subsequently, carbon dioxide

67,200-1130  
2002-1331

214 is flown from a first holding tank 200 through a first conduit 202 that connects to a second holding tank 204 through a second conduit 203. The second holding tank 204 holds a chemical substance 190 that increases the solubility of the carbon dioxide 214, by actuation of a first pump 206 of the first conduit 202 to flow a carbon dioxide/chemical substance mixture 226 into the supercritical critical cleaning chamber 208 at a flow rate of 0.2-0.6 liter/min. The pressure in the first holding tank 200 is 25-35 ATM, and the temperature is room temperature, while the carbon dioxide 214 is supplied in a liquid state. A second pump 207 is in fluid communication with the second storage tank 204 for pumping the chemical substance 190 to improve solubility of the carbon dioxide 214 into the supercritical cleaning chamber 208 in order to increase the cleaning capacity of the carbon dioxide 214. The chemical substance 190 that improves the solubility of the carbon dioxide 214 may be methanol,  $H_2O_2$ , benzene or other non-conductive additives.

[0039] The flowing process for the carbon dioxide 214 into the supercritical cleaning chamber 208 is continued until the carbon dioxide 214 fills up the cleaning chamber 208. The pressure and temperature are increased in the supercritical cleaning chamber 208 such that the carbon dioxide 214 in the

67,200-1130  
2002-1331

supercritical cleaning chamber 208 is maintained in a supercritical state: at a temperature of 310-500 degrees C and a pressure of 1500-1000 psi. The density of the carbon dioxide 214 in the supercritical cleaning chamber 208 is 500-900 kg/m<sup>3</sup>. The carbon dioxide 214 in the supercritical cleaning chamber 208 circulates inside the chamber 208 to improve the cleaning effect. The circulation speed inside the chamber 208 is 0.5-3 meter/sec.

[0040] After the cleaning process is completed, the spent carbon dioxide 214a is flown through a third conduit 210, which connects the supercritical cleaning chamber 208 to a recycle system 212, into the recycle system 212, by actuation of a pump 211. Re-usable carbon dioxide 214b is flown through a fifth conduit 215 that connects between the recycle system 212 and the first storage tank 200 and pumped by the fourth pump 222 into the first storage tank 200 for continued use. The un-usable carbon dioxide 214c is flown through a fourth conduit 225 that connects between the recycle system 212 and a heated exhaust system 216 and pumped by the third pump 220 into the heated exhaust system 216 for exhausting. After the cleaning steps are completed, the substrate 300 is removed from the cleaning chamber 208 wherein the metal surface of the substrate 300 is cleaned by the supercritical cleaning procedure and the

67,200-1130  
2002-1331

contaminating particles produced during the planarization of the conductive layer are removed.

[0041] Some of the supercritical fluids, other than carbon dioxide, that may be used in the method of the invention may include, but are not limited to:  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ; aqueous solutions of  $\text{NH}_3$ ; and  $\text{N}_2\text{O}$ ,  $\text{CH}_3\text{F}$ , and  $\text{CH}_2\text{F}_2$ . For  $\text{CH}_4$ , the supercritical solutions are -100 degrees C to -50 degrees C for temperature and 20 bar to 60 bar for pressure; for  $\text{C}_2\text{H}_6$ , the supercritical conditions are -15 degrees C to -50 degrees C for temperature and 20 bar to 60 bar for pressure; for  $\text{C}_3\text{H}_8$ , the supercritical conditions are 80 degrees C to 120 degrees C for temperature and 30 bar to 60 bar for pressure; for aqueous solutions of  $\text{NH}_3$ , the supercritical conditions are 100 degrees C to 150 degrees C for temperature and 100 bar to 130 bar for pressure; for  $\text{N}_2\text{O}$ , the supercritical conditions are 20 degrees C - 50 degrees C for temperature and 50 bar - 90 bar for pressure; for  $\text{CH}_3\text{F}$ , the supercritical conditions are 30 degrees C to 60 degrees C for temperature and 30 bar to 80 bar for pressure; and for  $\text{CH}_2\text{F}_2$ , the supercritical conditions are 60 degrees C to 100 degrees C for temperature and 40 bar to 80 bar for pressure.

[0042] While the preferred embodiments of the invention have been described above, it will be recognized and understood that

67,200-1130  
2002-1331

various modifications can be made to the invention and the appended claims are intended to cover all such modifications which may fall within the spirit and scope of the invention.